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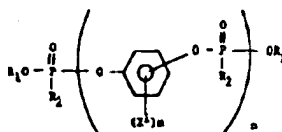
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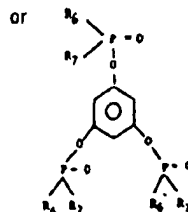
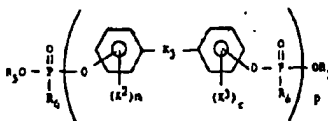
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(54) Flame retardant polyphenylene ether compositions

(57) There are provided flame retardant thermoplastic compositions suitable for molding, the compositions comprising a normally flammable polyphenylene ether resin, with or without a styrene resin, and a flame retardant amount of a flame retardant agent having the formula:



or



or mixtures thereof, wherein R₁, R₂ and R₃ are, independently, hydrocarbon, R₃, R₄, R₅ and R₆ are, independently, hydrocarbon or hydrocarbonoxy, X¹, X² and X³ are halogen, m and r are 0 or integers from 1 to 4 and n and p are from 1 to 30. In Examples bisphenol-A bisphosphate, bisphenol-A polyphosphate and hydroquinone bisphosphate and added to poly(2,6-dimethyl-1,4-phenylene)ether alone and blended with a rubber-modified high-impact polystyrene.

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SPECIFICATION

Flame retardant polyphenylene ether compositions

5 This invention relates to flame retardant polyphenylene ether compositions, and more particularly, to polyphenylene ether compositions which include novel flame retardant agents selected from among certain di- and polyfunctional phosphorus compounds. In comparison with corresponding compositions based on the use of mono-functional, low molecular weight phosphorus containing flame retardant agents, such as triphenyl phosphate, the compositions of this invention provide higher heat deflection temperatures, as well as enhancements in other properties not related to flame retardancy such as tensile strength and plate-out resistance. 10

Background of the Invention.—The use of thermoplastic materials in the formation of shaped articles by compression molding, extrusion, blow molding, and the like is well known. Of particular interest herein are the polyphenylene ether resins, alone or in combination with styrene resins. The polyphenylene ether resins are described, for instance, in Hay, U.S. 3,306,874 and 3,306,875 and in Stamatoff, U.S. 3,257,357 and 3,257,358, the disclosures of which are incorporated herein by reference. Compositions comprising a polyphenylene ether resin in combination with a styrene resin, modified or unmodified, are disclosed in Cizek, U.S. 3,383,453, incorporated herein by reference. Such thermoplastic compositions are known to be moldable to shaped articles having good overall properties. 20

A major shortcoming in the use of many thermoplastic resins, including polyphenylene ether resins and styrene resins, is their normally flammable nature. In applications where flame resistance is desired, such as in the fields of home construction, automobile and aircraft manufacture, packaging, electrical equipment, furniture, upholstery, and the like, to name just a few, flame extinguishing or retardant agents and/or drip retardant agents are commonly employed with the normally flammable thermoplastic resin or resins. 25

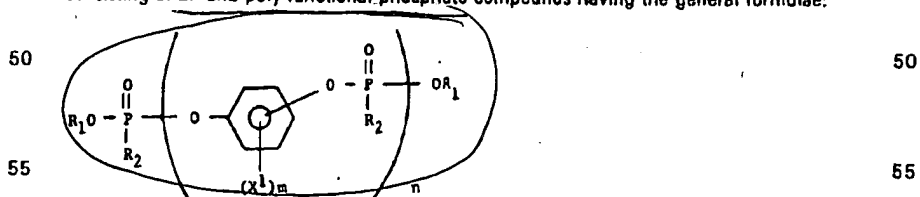
The uses of various antimony-, halogen-, phosphorus-, and nitrogen-containing compounds as flame retardant agents for flammable thermoplastic resins have been proposed in the art. For instance, the use of aromatic phosphates, such as triphenyl phosphate, as such or modified with other compounds, e.g., a halogenated aromatic, as a flame retardant for polyphenylene ether resins has been proposed. 30

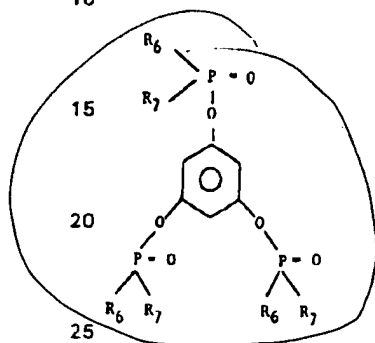
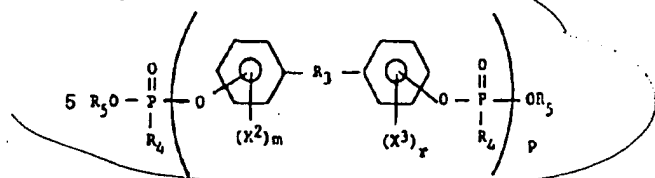
It has now been discovered that certain di- and polyfunctional phosphorus containing compounds are useful as flame retardant agents in compositions comprising a polyphenylene ether resin with or without a styrene resin. Besides being flame retardant, the compositions of this invention provide unexpected enhancements in other properties such as heat deflection temperature, tensile strength and plate-out resistance. 35

The increased resistance to plate-out provided by this invention is especially noteworthy. "Plate-out" as used in the art refers to the tendency of many flame retardant agents to migrate to the surface of the molten resin during molding. In such instances, the flame retardant agent often adheres to the inside surface of the mold which, in turn, necessitates frequent stoppages for cleaning. With the compositions of this invention, the incidence of plate-out is sharply reduced and molding equipment can be used for longer periods of time without cleaning. 40

Description of the Invention.—In its broadest aspects, this invention comprises flame retardant thermoplastic compositions which comprise:

- 45 (a) a normally flammable polyphenylene ether resin with or without a styrene resin; and
(b) a flame retardant amount of a flame retardant agent selected from the group consisting of di- and poly-functional phosphate compounds having the general formulae:





and mixtures thereof, wherein R_1 , R_2 and R_3 are, independently, hydrocarbon, R_4 , R_5 and R_6 are, independently, hydrocarbon or hydrocarbonoxy, X^1 , X^2 and X^3 are halogen, m and r are 0 or integers from 1 to 4, and n and p are from 1 to 30.

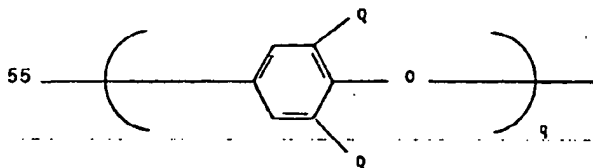
As used herein, the term "normally flammable" defines materials which do not meet the V-1 requirement of the Underwriters' Laboratories Bulletin No. 94 flame test.

Preferably, within the above general formulae, R_1 and R_2 are, independently, phenyl or alkyl of from 1 to 6 carbon atoms, R_3 is phenylene or alkylidene of from 1 to 6 carbon atoms, and R_4 , R_5 and R_6 are, independently, phenyl, alkyl of from 1 to 6 carbon atoms, phenoxy or alkoxy of from 1 to 6 carbon atoms.

The flame retardant agents of this invention can be prepared using known techniques, starting with commercially available materials. In general, they are prepared by reacting a halogenated phosphate compound with a phenol until the desired number of phosphate functional units are obtained. Under such conditions, the ratio of the phenol to halogenated phosphate compound will determine the number of repeating phenol-phosphate units, the greater the stoichiometric excess of phenol to halogenated phosphate compound resulting in a higher number of repeating units.

The phenols can be selected from among a wide variety of dihydric and trihydric phenolic compounds. By way of illustration, these include dihydroxyaromatic compounds such as hydroquinone(1,4-dihydroxybenzene), resorcinol(1,3-dihydroxybenzene), 2,2-bis(4-hydroxyphenyl)propane [bisphenol-A], 2,2-bis(4-hydroxyphenyl)pentane, 3,3-bis(4-hydroxyphenyl)pentane, 1,1-bis(4-hydroxyphenyl)ethane, and the like, and trihydroxy-aromatic compounds such as pyrogallol(1,2,3-trihydroxybenzene) and phloroglucinol(1,3,5-trihydroxybenzene).

The normally flammable polyphenylene ether resin is preferably of the type having the structural formula:



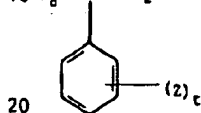
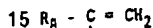
wherein the oxygen ether atom of one unit is connected to the benzene nucleus of the next adjoining unit, q is a positive integer and is at least 50, and each Q is a monovalent substituent selected from the group consisting of hydrogen, halogen, hydrocarbon radicals free of a tertiary alpha-carbon atom, halohydrocarbon radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus, hydrocarbonoxy radicals and halohydrocarbonoxy radicals

having at least two carbon atoms between the halogen atom and the phenyl nucleus.

A more preferred class of polyphenylene ether resins for the compositions of this invention includes those of the above formula wherein each Q is alkyl, most preferably, having from 1 to 4 carbon atoms. Illustratively, members of this class include poly(2,6-dimethyl-1,4-phenylene-
 5 ether); poly(2,6-dimethyl-1,4-phenylene)ether; poly(2-methyl-6-ethyl-1,4-phenylene)ether; po-
 ly(2-methyl-6-propyl-1,4-phenylene)ether; poly(2,6-dipropyl-1,4-phenylene)ether; poly(2-ethyl-6-
 propyl-1,4-phenylene)ether; and the like.

Especially preferred is poly(2,6-dimethyl-1,4-phenylene)ether, preferably having an intrinsic
 10 viscosity of about 0.45 deciliters per gram (dl./g.) as measured in chloroform at 30°C.
 The preparation of the polyphenylene ether resins is described in the aforementioned Hay and
 Stamatoff patents.

The preferred styrene resins will be those having at least 25% by weight of repeating units
 derived from a vinyl aromatic compound of the formula:



wherein R_8 is hydrogen, (lower) alkyl or halogen; Z is vinyl, hydrogen, halogen or (lower) alkyl;
 and t is 0 or an integer of from 1 to 5. Herein, the term "(lower) alkyl" means alkyl of from 1
 to 6 carbon atoms.

25 The term "styrene resin" as used broadly throughout this disclosure includes, by way of
 example, homopolymers such as polystyrene and polychlorostyrene as well as polystyrenes
 which have been modified by natural or synthetic rubber, e.g., polybutadiene, polyisoprene,
 butyl rubber, EPDM rubber, ethylenepropylene copolymers, natural rubber, polysulfide rubbers,
 polyurethane rubbers, epichlorohydrin, and the like, styrene containing copolymers such as the
 30 styrene-acrylonitrile copolymers (SAN), styrene-butadiene copolymers, styrene-maleic anhydride
 copolymers, styrene-acrylonitrile-butadiene terpolymers (ABS), poly- α -methylstyrene, copolymers
 of ethylvinylbenzene and divinylbenzene, and the like; block copolymers of the A-B-A and A-B
 type wherein A is polystyrene and B is an elastomeric diene, e.g., polybutadiene, radial teleblock
 copolymers of styrene and a conjugated diene, acrylic resin modified styrene-butadiene resins
 35 and the like, and blends of homopolystyrene and copolymers of the aforementioned type.

The polyphenylene ether resin and styrene resin are combinable in all amounts.
 The amount of flame retardant component (b) is not critical, so long as it is present in a
 minor, effective amount based on the weight of the resinous components—major proportions
 may detract from physical properties. In general, amounts from about 1 to about 30, preferably
 40 from about 5 to about 15 parts by weight of component (b), based on the weight of
 components (a), are employed.

The compositions of the invention can also further include reinforcing agents, preferably
 fibrous glass reinforcements, alone or in combination with non-glass reinforcing fillers. The
 fibrous glass is, especially preferably, fibrous glass filaments comprised of lime-aluminum
 45 borosilicate glass which is relatively soda free, known as "E" glass. However, other glasses are
 useful where electrical properties are not so important, e.g., the low soda glass known as "C"
 glass. The filaments are made by standard processes, e.g., by steam or air blowing, flame
 blowing and mechanical pulling. The preferred filaments for plastics reinforcement are made by
 mechanical pulling. The filament diameters range from about 0.000112 to 0.00075 inch, but
 50 this is not critical to the present invention.

In general, best properties will be obtained if the sized filamentous glass reinforcements
 comprise from about 1 to about 80% by weight based on the combined weight of glass and
 polymers and preferably, from about 10 to about 50% by weight. Especially preferably, the
 glass will comprise from about 10 to about 40% by weight based on the combined weight of
 55 glass and resin. Generally, for direct molding use, up to about 50% of glass can be present
 without causing flow problems. However, it is useful also to prepare the compositions containing
 substantially greater quantities, e.g., up to 70 to 80% by weight of glass. These concentrates
 can then be custom-blended with blends of resins that are not glass-reinforced to provide any
 desired glass content of a lower value.

60 Other ingredients, such as stabilizers, pigments, plasticizers, antioxidants, drip retardant
 agents, and the like, can be added for their conventionally employed purposes.

The manner in which the present compositions are prepared is not critical and conventional
 methods can be employed. Preferably, however, each of the ingredients is added as part of a
 blend premix, and the latter is passed through an extruder, at an extrusion temperature of from
 65 about 450 to about 600°F., dependent on the needs of the particular composition. The strands

emerging from the extruder may be cooled, chopped into pellets and molded to any desired shape.

Description of the Preferred Embodiments.—The following examples are illustrative of the compositions of this invention. They are not intended to limit the invention in any manner.

5

EXAMPLES 1-2

Flame retardant compositions according to this invention are prepared by tumbling 60 parts by weight of poly(2,6-dimethyl-1,4-phenylene)ether, having an intrinsic viscosity of 0.45 deciliters per gram in solution in chloroform at 30°C., 40 parts by weight of a styrene resin (FG 834, Foster-Grant Co., a small rubber-particle high impact polystyrene), 1.5 parts by weight of polyethylene, 0.5 part by weight of tridecylphosphite, 0.15 part by weight of zinc sulfide, 0.15 part by weight of zinc oxide and 12 parts by weight of a flame retardant agent as shown in Table 1, passing the blend through a 28 mm Werner-Pfleiderer twin screw extruder set at 580°F., with 20-25 inch-Hg vacuum-venting, and injection molding the extrudate on a 3 oz. Newbury machine at a cylinder temperature of 525°F. (set) and a mold temperature of 190°F. (set).

For purposes of comparison, a composition according to the prior art is prepared using the same ingredients in the same amounts, except that triphenyl phosphate is used as the flame retardant agent.

The molded compositions are evaluated for physical properties according to ASTM standards and for flame retardancy using the U.L. Bulletin No. 94 flame test. The results are summarized in Table 1.

TABLE 1. Flame Retardant Compositions Comprising a Polyphenylene Ether Resin, a Rubber-Modified High-Impact Styrene Resin and Flame Retardant Agent

EXAMPLE	1	2	A*
Flame retardant agent	bisphenol-A bisphosphate	bisphenol-A polyphosphate	triphenyl phosphate
<i>Properties</i>			
Heat deflection temp., °F.	237	247	210
UL-94 Self-extinguishing times, sec./sec.			
(a) test specimen size, inches	2/6, 9/1, <1/5	2/5, 1/5, 3/3	-
1/8 x 1/2 x 2 1/2			
(b) test specimen size, inches	3/12, 5/27, 4/6, 5/15, 15/3	11/13, 8/26, 9/8, 6/5, 10/11	3/2, 3/8, 1/7, 9/6, 1/2
1/16 x 1/2 x 5			
Notched Izod impact strength, ft.lbs./in.n.	4.8	4.9	6.6
Tensile elongation, %	72	97	55
Tensile strength at yield, psi	10,400	10,400	8,400
Tensile strength at break, psi	9,000	10,000	8,000

* comparison experiment

EXAMPLE 3

Using the procedure described in Examples 1-2, a flame retardant composition comprising 60 parts by weight of poly(2,6-dimethyl-1,4-phenylene)ether, intrinsic viscosity 0.45 dl/g in chloroform at 30°C., 40 parts by weight of a rubber modified high impact styrene resin (FG 834, Foster-Grant Co.), 12 parts by weight of bisphenol-A bisphosphate flame retardant agent, 1.5 parts by weight of polyethylene, 0.5 parts by weight of tridecylphosphite, 0.15 part by weight of zinc sulfide, 0.15 part by weight of zinc oxide and 0.5 part by weight of carbon black.

For comparison purposes, a composition according to the prior art is prepared using the same ingredients in the same amounts, except that triphenyl phosphate is used as the flame retardant agent. The physical properties of the compositions are summarized in Table 2.

TABLE 2. Flame Retardant Compositions Comprising a Polyphenylene Ether Resin, a Rubber Modified High Impact Styrene Resin and a Flame Retardant Agent

5 EXAMPLE	3	8*	5
Flame retardant agent	bisphenol-A bisphosphate	triphenyl phosphate	
<i>Properties</i>			
10 Heat deflection temp., °F.	239	204	10
UL-94 Self-extinguish- ing times, sec./sec.			
(a) test specimen	7/10, 7/17.	2/6, 2/4.	
15 size, inches	16/9, 6/8.	2/4, 2/2.	15
1/16 x 1/2 x 5	6/2	6/3	
Tensile elongation, %	69	84	
Tensile strength at yield, psi	9,500	7,500	
20 Tensile strength at break, psi	8,300	7,100	20
Degree of Plate-out	Light (sig- nificantly less than comparison experiment)	Heavy	
25			25

* comparison experiment

- 30 The "degree of plate-out" is determined by injection molding fifteen consecutive "short-
shots" (the molding material is allowed to only partially fill the mold) under the specified
molding conditions. A "full shot" is run immediately after the short-shot, in order to pick up the
"plated-out" flame retardant residue deposited on the inside surface of the mold. The molding
temperatures are 580°F. (cylinder) and 180°F. (mold); the total molding cycle is 40 seconds
35 from injection to removal of the part from the mold. The molded part is a plaque having the
dimensions 1/8 inch x 3 inches x 6 inches.

EXAMPLES 4-5

- 40 Flame retardant compositions according to this invention are prepared by forming a preblend
of the ingredients, passing the blend through a 28 mm Werner-Pfleiderer twin-screw extruder
set at 500-540°F., with no vacuum-venting, and injection molding extrudate on a 3 oz.
Newbury molding machine at 540°F. (set) cylinder temperature and 190°F. (set mold tempera-
ture.

- 45 The ingredients and physical properties of the respective compositions are summarized in
Table 3.

TABLE 3. Flame Retardant Compositions Comprising a Polyphenylene Ether Resin and a Flame Retardant Agent

5	EXAMPLE	4	C*	5	D*	5
	Ingredients,					
	parts by weight					
10	poly(2,4-dimethyl-1,4-phenylene) ether	75	75	85	85	10
	bisphenol-A-bisphosphate	25	-	15	-	
	triphenylphosphate	-	25	-	15	
15	Properties					15
	Heat deflection temp., °F.	250	205	289	267	
	UL-94 Self-extinguishing times, sec./sec.					
20	(b) test specimen size, inches	1/3, 2/4, 1/3, 1/3, 1/16 x 1/2 x 5	0/2, 1/1, 0/3, 1/3, 0/2	6/3, 1/6, 3/5, 1/4, 1/2	1/3, 0/2, 1/2, 1/4, 0/3	20
	Izod impact strength, ft.lbs./in.n.	0.8	0.7	0.8	1.1	
25	Tensile elongation, %	25	93	37	78	25
	Tensile strength at yield, psi	13,600	9,500	13,100	11,600	
	Tensile strength at break, psi	9,700	9,500	9,800	11,300	
30						30

* comparison experiment

EXAMPLE 6

A flame retardant composition according to this invention is prepared by forming a pre-blend of 55 parts by weight of poly(2,6-dimethyl-1,4-phenylene)ether, intrinsic viscosity 0.45 dl/g. in chloroform at 30°C., 45 parts by weight of a rubber modified high impact polystyrene (FG 834, Foster-Grant Co.), 4 parts by weight of hydroquinone bisphosphate flame retardant agent, 1.5 parts by weight of polyethylene, 1.0 part by weight of tridecylphosphite 0.15 part by weight of zinc sulfide and 0.15 part by weight of zinc oxide, passing the blend through a 28 mm Werner-Pfleiderer twin-screw extruder at 575°F., with 25 in.-Hg vacuum venting, and injection molding the extrudate on a 3 oz. Newbury machine at 530°F. (set) cylinder temperature and 190°F. (set) mold temperature.

For purposes of comparison, a corresponding prior art composition using triphenyl phosphate as the flame retardant agent is also prepared and molded using the same conditions. The physical properties of the respective compositions are summarized in Table 4.

TABLE 4. Flame Retardant Compositions Comprising a Polyphenylene Ether Resin, Rubber Modified High Impact Styrene Resin and a Flame Retardant Agent

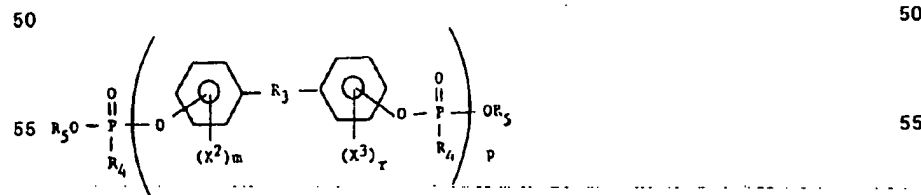
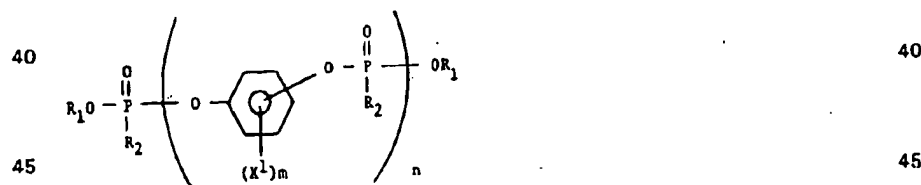
5 EXAMPLE	6	E*	5
Flame retardant agent	hydroquinone-bisphosphate	triphenylphosphate	
<i>Properties</i>			
10 Heat deflection temp., °F.	251	242	10
UL-94 Self-extinguishing times, sec./sec.			
(a) test specimen size, inches	9/6, 6/8, 14/15, 10/7, 16/8	4/9, 14/11, 21/6, 7/5, 17/15	15
15 1/8 x 1/2 x 2 1/2 Izod impact strength, ft.lbs./in.n.	2.7	3.8	
Tensile elongation, %	58	93	
20 Tensile strength at yield, psi	10,300	9,400	20
Tensile strength at break, psi	8,900	9,100	
25 * comparison experiment			25

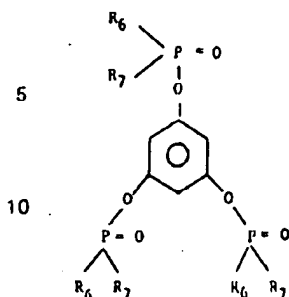
Obviously, other modifications and variations of the present invention are possible in the light of the above disclosure. It is, therefore, to be understood that changes may be made in the particular embodiments described above which are within the full intended scope of the invention as defined in the appended claims.

CLAIMS

1. A flame retardant thermoplastic composition which comprises:

- (a) a normally flammable polyphenylene ether resin with or without a styrene resin, and
(b) a flame retardant amount of a flame retardant agent selected from the group consisting of di- and polyfunctional phosphate compounds having the general formula:





and mixtures thereof, wherein R_1 , R_2 and R_3 are, independently, hydrocarbon, R_4 , R_5 and R_7 are, independently, hydrocarbon or hydrocarbonoxy, X^1 , X^2 and X^3 are halogen, m and r are 0 or integers from 1 to 4, and n and p are from 1 to 30.

2. A composition as defined in Claim 1 wherein R_1 and R_2 are, independently, phenyl or alkyl of from 1 to 6 carbon atoms, R_3 is phenylene or alkylidene of from 1 to 6 carbon atoms, and R_4 , R_5 and R_7 are, independently, phenyl, alkyl of from 1 to 6 carbon atoms, phenoxy or alkoxy of from 1 to 6 carbon atoms.

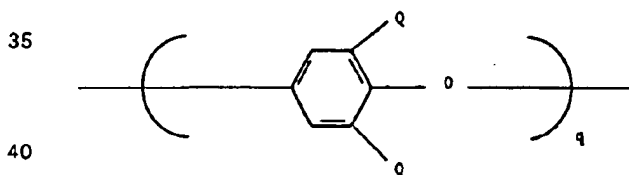
3. A composition as defined in Claim 1 wherein said flame retardant agent is bisphenol-A bisphosphonate.

4. A composition as defined in Claim 1 wherein said flame retardant agent is bisphenol-A polyphosphonate.

5. A composition as defined in Claim 1 wherein said flame retardant agent is hydroquinone bisphosphonate.

6. A composition as defined in Claim 1 wherein said flame retardant agent is present in an amount of from about 1 to about 30 parts of (a).

7. The composition of Claim 1 wherein the polyphenylene ether resin of (a) has the formula:



wherein the oxygen ether atom of one unit is connected to the benzene nucleus of the next adjoining unit, q is a positive integer and is at least 50, and each Q is a monovalent substituent selected from the group consisting of hydrogen, halogen, hydrocarbon radicals free of a tertiary alpha-carbon atom, halohydrocarbon radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus, hydrocarbonoxy radicals and halohydrocarbonoxy radicals having at least two carbon atoms between the halogen atom and the phenyl nucleus.

8. The composition of Claim 7 wherein the polyphenylene ether resin is poly(2,6-dimethyl-1,4-phenylene)ether.

9. The composition of Claim 1 wherein a styrene resin is present.

10. The composition of Claim 9 wherein the styrene resin is a rubber modified high impact polystyrene.

11. The composition of Claim 1 which includes a reinforcing amount of a reinforcing filler.

12. A composition as defined in Claim 1 and substantially as hereinbefore described with reference to any of Examples 1 to 6: